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Atmospheric Chemistry and Physics Discussions

Interactive comment on "NO_2 climatology in the northern subtropical region: diurnal, seasonal and interannual variability" *by* M. Gil et al.

Anonymous Referee #1

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Referee comment on 'NO2 climatology in the northern subtropical region: diurnal, seasonal and interannual variability' by M. Gil et al.

This is an interesting article, with a number of impressive results. The agreement between the observed diurnal variation of total column NO2 and that simulated by a stacked model on top of SLIMCAT is convincing. The comparison between the ground-based and satellite data is a nice demonstration of the use of and need for reliable validation measurements. The comparisons between observed and modelled annual cycles of sunset and sunrise NO2 are illustrative, confirming what we know about ERA40 windfields, and demonstrating the use of data assimilation as a technique to improve our understanding of the atmospheric chemistry. The figures are very nice.

The paper could be improved in a number of places. An important shortcoming is that the authors do not provide a mechanistic explanation for the signature of upper stratospheric temperature present in the observed seasonal evolution of the NO2 cycle. I think the authors should tell us whether or not (and if so, how) JNO2, k1, and/or k2 change with temperature, and whether this is consistent with the 6% total column effect that they observe. The only other shortcoming I find is that sometimes important quantitative information is not given, and that a number of textual aspects could be improved on considerably. For example, in quite a number of places, abbreviations, concepts, and instruments are being brought up without having been defined or introduced. Once these issues are resolved, this paper should be published in ACP.

Specific comments

Abstract, line 7: suggest replacing 'source' by 'sources'.

Abstract, lines 13-15: suggest mentioning what years this study concerns.

Abstract, line 18-19: I suggest specifying what 'significantly' is in quantitative terms.

P15069, line 4: contribution of what?

P15069, line 5: suggest replacing 'mid' by 'middle'.

P15069, line 16: I think 'and' should be removed before 'with a'.

P15069, lines16-18: I think it would be more clear if the authors would mention the modelled trend instead of making a relative statement against the observed trend.

P15069, line 27: suggest mentioning NDACC web link here.

P15070, line 3: recommend spelling out the abbreviation before using 'SAOZ', and providing SAOZ web link, same for 'BREDOM'.

P15070, lines 9-11: This statement is true if only one sensor is used. A combination of two satellite instruments with different local overpass times, for instance SCIAMACHY

ACPD

7, S6731–S6737, 2007

Interactive Comment

and OMI, allows for a comparison of NO2 columns if both instruments observe the location under cloud-free conditions on the same day. In fact, a paper on this subject has recently been accepted for publication in the Journal of Geophysical Research (Boersma, K. F., D. J. Jacob, H. J. Eskes, R. W. Pinder, J. Wang, and R. J. van der A (2007), Intercomparison of SCIAMACHY and OMI tropospheric NO2 columns: observing the diurnal evolution of chemistry and emissions from space, J. Geophys. Res., doi:10.1029/2007JD008816, in press.).

P15070, line 25: recommend mentioning what the 'recorded period' actually is.

P15071, lines 3-9: this formulation is awkward. What is 'the equivalent path for a given wavelength'? Do the authors mean the equivalent photon path? Please formulate more clearly. Also the sentence 'At twilight ... tropospheric one' has not been written clearly. Stratospheric contribution of what? What is a slant, tropospheric path? This should be rewritten, and I strongly recommend providing references to earlier work that did a good job describing zenith-sky DOAS observations.

P15071, line 12-15: it should be made clear that ratioing with a high sun spectrum instead of an extraterrestrial spectrum introduces a bias in the retrieved NO2. This is now fumbled away in lines 13-15 that state that the NO2 SCD (the concept of the SCD should be introduced here) is 'in fact' the DSCD. In fact, the NO2 SCD is the DSCD + an unknown bias! The authors acknowledge this later, at P15072, line 1, but it should be made clear here already.

P15071, eq. (4): I think I see what the authors want to do here, but the formulation needs to be improved. The authors want to find those parameters a, b, c, d, and Ni, that minimize the residuals between the observed (ratioed) spectra, and the modelled spectra. By differentiation with respect to the unknowns Ni and setting to zero, they will only find solutions for Ni, not for a-d. So where do the coefficients a-d come from? Furthermore the plus sign on the right hand side should be a minus sign or Lambert-Beer would not hold. The double use of brackets is awkward – why not using the proper

ACPD

7, S6731–S6737, 2007

Interactive Comment

EGU

symbol for minimization, i.e. the norm-symbol? Furthermore the summation should be over i absorbers/scatterers. Finally I suggest using a proper symbol for multiplication instead of a low dot.

I think it would be appropriate if the authors mention here which spectral fitting window and what set of reference spectra they use. What are typical values for shift and squeeze that they get? What is the theoretical precision of the NO2 slant column (random error)?

P15072, lines 4-5: I don't understand what O3 has to do with the reference spectrum bias correction.

P15072, lines 23-25: Interesting approach. Have the authors done more than just one calculation of the reference content? It would be reassuring if the authors had done so, and that the newer reference estimates would not differ too much from the original Langley plot result. Equation (6) should have a proper multiplication sign instead of a low dot. What is the typical reference content – does the number make sense?

P15073, line 8: 'constraint' should be 'constrained'.

P15073, lines 10-12: the fact that the station is under tropospheric conditions most of the time does not in itself prevent pollution from the coastal towns. I guess that the authors want to state that pollution from these towns has little chance of being sampled at Izana.

P15073, line 12: typo twilight.

P15073, lines 25-26: I suggest the authors provide a number here on the signal-to-noise ratio that they typically obtain.

P15074, I recommend that the authors also give a typical signal-to-noise for the advanced visible spectrograph. Also, on this page and later, the abbreviations EVA, RASA, and ARTIST have not been properly introduced. Now the reader has to guess whether EVA is the first of the two instruments contributing to the data record, RASAS

ACPD

7, S6731–S6737, 2007

Interactive Comment

EGU

the advanced visible spectrograph and so on. I suggest including a table with a brief overview of the three instruments and techniques here, including operational time period, S/N ratios, fitting windows, resolutions etc. would help here.

P15075, last line: 'van Roozendael' should be 'Van Roozendael'.

P15076, first line: what is a 'pseudo-cross-section'?

P15076, lines 19-20: I wonder why the authors do not mention that uncertainties in all cross-section spectra contribute to the error budget. Have they established that?

P15076, line 26: I recommend removing 'a' in 'on a realistic NO2 profiles'.

P15076, line 27: I suggest the authors clarify what a 'single AMF-set' is. The way I read it, it seems an AMF computation with one fixed AFGL-profile, and dependencies solely on viewing geometry. The 5% error would then be from not accounting for NO2 profile variability and another 4-5% error from non-sphericity in the radiative transfer model? If so, I suggest the authors clarify this.

P15075, line 9: suggest replacing 'temperature is larger' by 'temperature is higher'.

P15077, eq. (7): I suggest the authors provide a reference here.

P15077, lines15-22: Interesting discussion, and the results make sense. However, the cited 'uncertainty' is rather a systematic effect (the sign change is likely to occur with season), and should be treated accordingly, or the authors should convice the readers that the effect is truly random.

P15078, line 7: I suggest the authors explain what PDA stands for.

P15078, section 3.4: The authors present a very impressive result here with little difference between retrievals from two independent measurements. From here on, the authors could use ˜0.2 x 1015 molec.cm-2 as an upper limit for the random error component on their retrievals. Is this number consistent with the uncertainty they get from the DOAS fit? Because the retrievals are similar for the two instruments (same cross

ACPD

7, S6731–S6737, 2007

Interactive Comment

sections, same radiative transfer model, same temperature correction), the two retrievals may be expected to be biased in similar ways. Such a bias, if known, would justify a correction to the data, and I think it is misleading to state that because of 'these excellent results, no corrections have been applied to the data subsets'. I suggest that the authors remove this sentence and tell the reader that there is a possibility that the data is biased, and I even think they can easily come up with an upper limit for this bias (combining the estimates for cross sections 2%, radiative transfer 6-7%, and temperature 3% should give an idea).

P15079, line 15: suggest replacing 'tracer' by 'tracers'.

P15080. line 10: suggest mentioning for what local time the reference content holds (Figure 5 states 70 pm – should that be 70 degrees pm?).

P15080, line 14: I suggest explaining what 'adapted SLIMCAT box model' means. Is it the bias-correction of +0.3 1015 molec.cm-2?

P15080, section 5.1: how representative is Figure 5 for other days with little aerosol?

P15080, line 24-27: The asymmetry is not due to, but rather described with a secondary wave. I suggest the authors rephrase this.

P15081, lines 7-13: this all sounds plausible, but I think the authors should tell us whether and how JNO2, k1, and/or k2 change with temperature.

P15082, line 9: I suggest adding that there is a lack of simultaneity between *ground-based and satellite* measurements.

P15082, lines 13-16: the comparison of GOME to Izana ground-based NO2 column provides interesting information on the details of the diffuser plate correction – I recommend the authors discuss this a little bit more. Judging from Fig. 10, the assumption of constant 2.0 1015 molec.cm-2 over the Pacific region is mostly in error in the later months of the year and not so much in Jan-Feb-Mar. Is this consistent with knowledge about the monthly variability of NO2 columns in the Pacific reference box from

SCIAMACHY that does not suffer from such errors?

P15085, line 6: here, for the first time, the overall error budget of 10-12% is being mentioned. This should already have been done.

P15086, line 3-5: I suggest replacing ’points to’ by ’confirms previously established’.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 15067, 2007.